09/621,746

PATENT
255/236US
P00-0036US2
54008-8064.US01

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Eric J. Bergman	EXAMINER: Z. EL-ARINI
SERIAL NO.: 09/621,028	GROUP ART UNIT: 1746
FILED: JULY 21, 2000	CONF. NO.: 4066
FOR: PROCESS AND APPARATUS FOR TREATING A WORKPIECE SUCH AS A SEMICONDUCTOR WAFER	

Transmittal Letter

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

1. Transmitted herewith are the following:

- [x] Amendment
- [ ] A Petition for a one-Month Extension of Time
- [ ] A Terminal Disclaimer
- [ ] Sequence Listing printout, floppy diskette, matching declaration
- [ ] Information Disclosure Statement, Form 1449, References
- [x] A return postcard

2. Entity Status

- [ ] Small Entity Status (37 CFR 1.9 and 1.27) has been established by a previously submitted Small Entity Statement.

3. Conditional Petition for Extension of Time:

An Extension of Time is requested to provide for timely filing if necessary for timely filing of this transmittal and enclosures.

Certificate of Mailing

I hereby certify that this paper (along with any referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage in an envelope addressed to the Assistant Commissioner for Patents, Washington, DC 20231.

November 4, 2002
Date of Deposit

Debbie Gilbert
Debbie Gilbert

[54008-8064/LA023050.113]

4. Fees

The fees for claims have been calculated as shown below:

For:	No. Filed	No. Extra	Large Entity	
			Rate	Fee
Total Claims	26 – 26	0	x $ 18 =	$ 0
Independent Claims	5 – 4	1	x $ 84 =	$ 84.00
☐ Multiple Dependent Claim Presented			+ 270 =	$ 0
		Amount paid today		**$ 84.00**

5. Fee Authorization

☒ A check in the amount of $84.00 is enclosed to cover the Filing Fee. The Commissioner is hereby authorized to charge any deficiency in fees under 37 CFR 1.16 and 1.17 to Deposit Account No. **50-0665**.

☐ Please charge the Filing Fee and any other fees necessary for timely filing of this application to Deposit Account No. **50-0665**.

☐ ***Filing fee to be submitted in response to anticipated receipt of Notice to File Missing Parts. DO NOT CHARGE DEPOSIT ACCOUNT.**

Respectfully submitted,
Perkins Coie LLP

Date: Nov. 4, 2002

By: Kenneth H Ohriner
Kenneth H. Ohriner, Reg. No. 31,646

34055
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FOR: PROCESS AND APPARATUS FOR TREATING A WORKPIECE SUCH AS A SEMICONDUCTOR WAFER

#12
12-12-02

RESPONSE

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

The following is Applicant's response to the Office Action mailed August 2, 2002.

REMARKS

Claims 1-24, 26, and 27 are in the application. Reconsideration of withdrawal of the rejections is requested in view of the following remarks.

The claims describe novel methods for cleaning workpieces or semiconductor wafers. As described in the specification at pages 1-4, the conventional "RCA" clean process has various disadvantages. It requires numerous discreet steps, which increases equipment costs, space and labor requirements, as well as process time. It also consumes relatively larger amounts of chemicals which may not be easily disposed of. These disadvantages of the RCA clean are well known in the art (see Li et al., U.S. Patent No. 5,749,975, column 1, lines 34-66, of record).

The claims describe improved cleaning methods involving the use of both heat, a liquid layer on the surface of the workpiece, and large amounts of ozone. As noted by the Examiner, individually, each of these elements may be found in the prior art. However, their use in combination, as claimed, is counterintuitive, and teaches away

from the prior art. On the one hand, it is well known that adding heat will increase the reaction kinetics of an oxidizer, thereby speeding up process times. However, on the other hand, it is also well known that the solubility of ozone (an oxidizer gas) decreases with increasing temperature. At e.g., 60°C, the solubility of ozone in water is just a small fraction of the solubility at room temperature. See Fig. 1 attached. Conversely, at cooler temperatures, the solubility is much greater. For example, the solubility of ozone in water at 10°C is about three times greater than the solubility at 20°C. This characteristic inverse function of gas solubility versus water temperature suggests the use of water at room temperature or lower, to increase the level of dissolved ozone in the water. Indeed, various prior art techniques using chilled ozonated water have been proposed. While these techniques can achieve high levels of dissolved ozone, reaction times remain low due to the low temperatures. On the other hand, using water at high temperatures is not effective due to the decreasing concentration of ozone in the water as temperature increases.

The claimed methods achieve the advantages of both high ozone availability and high temperature, to provide fast reaction times, by using diffusion, rather than dissolution. While only a low amount of ozone can be dissolved within the heated liquid layer on the surface of the workpiece, large amounts of ozone diffuse through the layer to react at the workpiece surface.

All of the claims describe introducing ozone at a rate of at least 90 gms/hour, a step not suggested in any of the prior art.

At the time the invention was made, the use of ozone at plus 90 gms/hour in wet processing of wafers, was unheard of. While ozone generators may have been able to create ozone at such a high rate, there was no interest in doing so in semiconductor manufacturing, since there was no way to use that much ozone. For example, with wet processing by immersion, a typical 20 liter immersion tank holds 20,000 gms of water. With the saturation point at about 20ppm, at 20 degrees C, .001gm of ozone gas could dissolve into the water. Any more ozone would not only be wasted as excess, but it would also have be destroyed before releasing (due to the reactive/corrosive

characteristics of ozone). Hence, if ozone were generated at 90 gms/hour, as claimed, a flow of 90,000 liters/hour of water would be needed to dissolve the ozone. This example demonstrates the larger amounts of ozone described in the claims.

The reason such extreme amounts of ozone are used is because in the claimed methods, the ozone is largely not dissolved at all. Rather, the ozone is diffused through the heated liquid layer on the wafer. As diffusion is the primary mechanism for facilitating reactions with ozone, the low solubility of ozone in the heated water is no longer a limitation on use of ozone.

Turning now in detail to the prior art, the principle reference, Li et al., no. 5,749,975 describes a dry cleaning process. Specifically, Li et al. teaches away from a wet cleaning process (as described in the pending claims) in favor of a dry-cleaning process, as described at columns 1 and 2 of Li et al. While the Examiner is correct that Li et al. discloses a surface diffusion layer at column 4, lines 18-60, the heated liquid layer in the pending claims is patentably distinct over Li et al. Initially, in Li et al., the diffusion layer is formed by depositing a vapor. Column 4, line 42. Since Li et al. is a dry-cleaning process, the vapor layer is necessarily extremely thin, with no likelihood or description of the diffusion layer assisting in maintaining the workpiece at an elevated temperature, as claimed. Moreover, in Li et al., the purpose of the diffusion layer is to inhibit direct reaction of the gas phase with the wafer. Column 4, line 33. This is done to eliminate surface roughness. Column 2, lines 38-46.

Hence, Li et al. does not disclose a heated liquid layer, as claimed. Although Li et al. mentions use of ozone, the claimed 90 gms/hour of ozone is not suggested in Li et al. Moreover, Li et al. says nothing about controlling a thickness of the heated liquid layer.

Perhaps more importantly, the intent of Li et al. runs opposite to the pending claims. The intent of Li et al. is to inhibit direct reaction of the gas phase with the wafer surface (column 4, line 33) or, in other words, to decrease the mean free path and create a smooth silicon surface, with less pitting or scoring. In contrast, the pending

claims increase the reaction rate, by increasing the amount of ozone reacting at the workpiece surface, through diffusion.

Kamikawa et al., U.S. Patent No. 6,299,696 B2, has a December 12, 2000, U.S. filing date. As the present application has a July 21, 2000, filing date (disregarding the priority claims) Kamikawa et al. is not prior art. While Kamikawa et al. claims priority to JP11-354785, filed in Japan on December 14, 1999, the foreign priority date of the reference cannot be used to antedate the filing date of the present application. MPEP 2136.03.

Matsuoka EP0548596A2 discloses use of ozone and rotation of the workpieces, as noted by the Examiner at page 3 of the 8/2/2002 office action. However, Matsuoka teaches away from heating, as follows:

> "A problem with a dry treatment using ozone is that when resists implanted at high doses are treated at relatively high temperatures, pumping, etc., takes place through heat, making some resist residues likely to remain intact." Page 2, lines 56-58.
>
> "Heating the substrates does not permit wet ozone to have well-enough effects, because any thin water film cannot occur even when a wet ozone-containing gas is fed." Page 3, lines 34-35.

In example 1, the water is 25°C. In comparative example 1, the water is 20°C. Consequently, Matsuoka does not suggest use of a heated liquid.

With respect to ozone consumption, in Matsuoka the suggested rate in Example 1 is about 25 gms/hour (based on the 6 lpm and 55,000 ppm parameters). The claims describe 90 gms/hour and up, i.e., a 350% increase over Matsuoka.

Based on the foregoing, the combination of Li et al., Bergman, and Matsuoka does not render the claims obvious, because the combination fails to suggest use of a heated liquid assisting in maintaining the workpiece at an elevated temperature; introducing ozone at at least 90gms/hour; or diffusion of the ozone through the heated liquid layer for reaction at the surface of the workpiece.

As the application is in addition for allowance, a Notice of Allowance is requested.

Respectfully submitted,
Perkins Coie LLP

Date: Nov. 4, 2002

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Ozone Solubility in H_2O as a Function of Temperature